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STUDIES OF STRESS-STRAIN BEHAVIOR OF SAN/GLASS BEAD COMPOSITES IN THE GLASSY REGION

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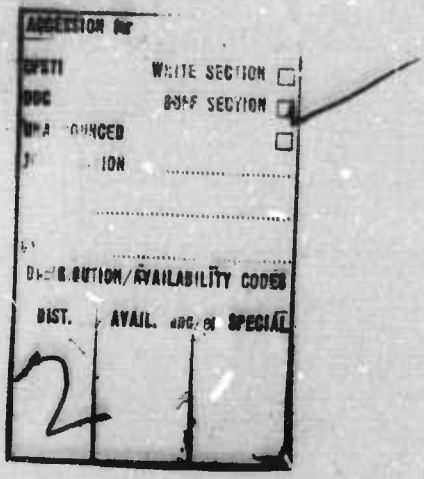

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HPC 70-120

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BY

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WASHINGTON UNIVERSITY

SEPTEMBER 1970

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FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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STUDIES OF STRESS-STRAIN BEHAVIOR OF SAN/GLASS BEAD COMPOSITES IN THE GLASSY REGION

L. Nicolais* and M. Narkis**
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St. Louis, Missouri 63130

ABSTRACT

The effects of temperature, strain rate and filler content on tensile properties of SAN/glass bead composites are studied. A point of discontinuity on the stress-strain curves for unannealed composites is investigated, annealing results in smooth curves with no break points. A simple model for the filler effect on yield stress is suggested and shown to be in a good agreement with experimental data. A double shifting procedure to account for the temperature and filler effects on yield stress as a function of strain rate is proposed. A single master curve that can be represented by the following equation:

$$\frac{\sigma_{yp}}{1 - 1.21\phi^{2/3}} = A + B \ln (\dot{\epsilon} a_T)$$

relates composite yield stress to strain rate, temperature and filler volume fraction.

*On leave from the Laboratorio di Ricerca su Tecnologia dei Polimeri e Reologia del C.N.R. Napoli, Italy.

**Presently with the Center for Industrial Research, POB 311, Haifa, Israel.

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STUDIES OF STRESS - STRAIN BEHAVIOR OF SAN/GLASS BEAD COMPOSITES IN THE GLASSY REGION

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Introduction

The mechanical behavior of unfilled plastics in the temperature range below their glass transition has been extensively studied. It is well known that the yield stress depends on temperature and strain rate [1] and that yield stress data at different temperatures and strain rates can be shifted to form a master curve [2]. Lohr [2] has shown that the yield stress of an unfilled polymer σ_{yp} plotted versus strain rate $\dot{\epsilon}$ at different temperatures can be shifted along the $\dot{\epsilon}$ axis and the master curve obtained may be represented by the following equation

$$\sigma_{yp} = K_1 + K_2 \ln (\dot{\epsilon}/\dot{\epsilon}_1) a_T \qquad (1)$$

where K_1 and K_2 are constants which depend on the reference temperature chosen and on the specific polymer, and $\dot{\epsilon}_1$ is equal to 1 in/in/min. The shift procedure has been recently confirmed by Ishai [3] for epoxy-versamid systems. Ishai has found that the yield strain is practically independent of strain rate and slightly dependent on temperature. The epoxy-versamid system was further studied [4] and the yielding phenomenon was interpreted by using Eyring's theory of non-Newtonian viscoplastic flow. Results on yield stress of PVC, polycarbonate and PMMA were presented by Zitek and Zelinger [5]. In their work σ_{yp} is plotted versus temperature over a wide temperature range and different regions that can be

described by straight lines are obtained. The transitions between two adjacent regions are sharp and can be related to dynamic dispersions, which exhibit the glass transition temperature or other secondary transitions. A detailed description of the temperature and strain rate dependence of the tensile yield strain of PMMA was recently published by Rusch and Beck [6].

A literature survey shows that only a few experimental data are available on the stress-strain behavior and yielding phenomenon of particulate systems in the glassy state. The stress-strain behavior of elastomeric/glass bead composites was studied by Smith [7]. Yield stress and yield strain were found to decrease with increasing glass bead concentration. The yield strain was found to depend strongly on temperature. Smith has also given a detailed description of stress-strain curves for the filled elastomers. Yield stress was also shown to decrease with filler concentration for PPO/glass beads composites [8]. Youngs modulus of these composites is known to increase with increasing the filler concentration and can be predicted [9, 10].

In the present work the stress-strain behavior of SAN (styrene-acrylonitrile copolymer)/glass b ads composites is studied at several different strain rates, temperatures and filler concentrations.

Experimental

Composites of styrene-acrylonitrile copolymer [11] (Lustran A, Monsanto Co.) and glass beads (Cataphote Corp. type 2740, diameter range 0.0005 to 0.0015") were prepared by milling and compression molding. The crude sheets from the two roll mill were cut and then molded in a 3 x 8 in. compression mold at 185°C under a pressure of 800 psi. The molded sheets were found to be very homogeneous by

burning small samples and calculating the content of glass beads. Typical variation was less than 0.2%. Specimens containing the following concentrations by volume of glass beads were prepared: 11.2, 21.3, 42.7 and 62.5%. In the present paper filler concentration is always expressed as volume concentration. The composite containing 62.5% glass beads had very low tensile or flexural strengths and was therefore discarded.

Tensile specimens (ASTM D638-64T) about 0.1 in. thick were cut from the molded sheets. These specimens were tested with constant rates of strain and constant temperatures with an Instron universal testing machine by using a strain gage extensometer (G-51-11).

Specimens were tested at 24, 48, 65 and 85°C and at strain rates of 0.00526, 0.0262, 0.131 and 0.526 min^{-1}.

Results and Discussion

Preliminary studies on the SAN/glass beads composites were carried out by using the Clash-Berg torsional stiffness tester. In Figure 1 shear modulus after 10 sec., G(10), is plotted versus temperature for different concentrations of glass beads. The modulus-temperature curves exhibit the significant effects of the glass beads on G(10) below and above the glass transition. Glass transition temperatures determined by DTA were 99, 102.5, 105 and 106°C for 0, 7.6, 20 and 43% glass beads respectively. Results on the behavior of the SAN/glass beads composites above their glass transition will be published elsewhere.

Typical stress-strain curves for the unfilled SAN under a constant strain rate and at different temperatures are shown in Figure 2. Young's modulus and the stress at break are shown to decrease with increasing the temperature. In the present

work yield stress is defined as the first point at which the tangent of the force-deformation curve becomes zero. With this definition the failure of the unfilled polymer is brittle (Figure 2).

This can also be seen by visual examination of the broken surfaces. However from the curvature of the stress-strain curves one can expect that the stresses at break of the unfilled polymer are not too far from the corresponding yield stresses.

The stress-strain curves are markedly changed by adding a filler even at rather low concentrations. In Figure 3 stress-strain curves for 11.2% glass-beads composites are shown. These curves show a definite yield point at all temperatures. The yield stress depends strongly on temperature but yield strain decreases only slightly with increasing the temperature. This is in agreement with literature data on unfilled epoxy-versamid systems [3]. Comparison of Figures 2 and 3 shows that at a given temperature, the composite yield stress is lower than the ultimate stress of the unfilled polymer. In Figure 3 a sharp break in the stress-strain curves at around 0.35% strain can be seen. This break has been found to be typical for all the composites studied in the present work, however, no break point can be found in the curves for the unfilled polymer (Figure 2). The stress at the point of discontinuity, σ_D, is temperature dependent and decreases as the temperature increases. The strain at the discontinuity, ϵ_D, is practically independent of temperature.

In Figure 4 are shown stress-strain curves for different concentrations of glass beads at a constant temperature and strain rate. The yield stress is shown to decrease significantly with increasing the bead concentration [8]. The yield strain is also dependent on the bead concentration and decreases with increasing volume fraction, in agreement with Smith's results [7] on elastomeric PVC composites. The stress

and strain at the disctoninuities are shown to be practically independent of the filler concentration, while the slope of the stress-strain curve above the discontinuity is strongly dependent on the bead concentration. Young's modulus increases with the filler concentration in agreement with Kerner's well known reinforcement theory [9].

In Figure 5, σ_D is plotted versus temperature for different concentrations of glass beads. σ_D is shown to be practically independent of the filler concentration and to decrease with increasing the temperature. Further analysis of additional stress-strain curves (not given here) for the SAN/glass beads composites has shown that for all practical purposes σ_D is temperature dependent but independent of strain rate and volume fraction of filler, while ϵ_D is independent of temperature, strain rate and volume fraction of filler.

A detailed qualitative description of stress-strain curves for filled elastomers was given by Smith [7]. His description of the shape of these curves also fits the stress-strain curves that were obtained with glassy composites in the present work. To further verify the generality of the discontinuity in the stress-strain curves, a few more experiments were carried out. PPO/glass bead and polystyrene/glass bead composites (20% beads) were tested at room temperature and similar discontinuities in the stress-strain curves were found for both materials, therefore, the break point is not a phenomenon typical only of SAN/ glass bead composites. A few loading -unloading experiments, on the SAN composites, where samples were loaded to stresses well above the break point but below the yield point and then released have shown almost total recovery of strain with only a small hysteresis. In other experiments involving loading-unloading-reloading it has been found that

the break point shows up again at practically the same stress and strain values. With these results it seems that no significant dewetting or other irreversible processes occur at the break point. This conclusion led to a few annealing experiments and completely smooth room temperature stress-strain curves were obtained for samples with 21.3% glass beads after 6 hrs. annealing at 95°C. The break point is undoubtedly an exhibitions of the state of internal stresses in the composite, however, a satisfactory physical explaination of the discontinuity phenomenon is not known at present. Young's modulus is affected by annealing and for samples of 21.3% beads the modulus is about 20% higher after annealing. Extremely careful annealing procedures are necessary if experimental moduli of composites are compared with predicted moduli obtained by different equations [9, 10, 12] since the differences between the equations are similar to the effect of annealing.

In Figure 6 a typical plot of yield stress versus strain rate at various temperatures is shown for 42.7% glass beads. The straight lines are parallel and can be easily shifted to produce a master curve. The shift parameter, a_T, is dependent on temperature. Figure 6 shows that the yield stress-strain rate-temperature relations are in agreement with Equation (1), verifying that the shift procedure for unfilled polymers [2, 3, 5, 8] applies also for the composites studied in the present work.

A simple theoretical analysis for the yield strain of elastomeric composites is given by Smith [7] as follows:

$$\epsilon = \epsilon_r(1 - 1.105\phi^{1/3}) \tag{2}$$

where ϕ is the volume fraction of filler, ϵ_r is the strain in the polymer and ϵ is the strain imposed on the composite. Nielsen [13] suggests the following equation

in the case of perfect adhesion between polymer and filler particles,

$$\epsilon_B \text{ (filled)} / \epsilon_B \text{ (unfilled)} \doteq 1 - \phi^{1/3} \tag{3}$$

and, the following equation for the yield stress in the case of no adhesion between polymer and filler

$$\sigma_B \text{(filled)} / \sigma_B \text{ (unfilled)} = (1 - \phi^{2/3})S \tag{4}$$

In these equations B stands for "Break" and S is a stress concentration function which may have a maximum value of 1.0 when there is no concentration. Generally S, according to Nielsen, is expected to have a value of the order of one-half. Equation (4) has not been checked with experimental data to the best knowledge of the authors probably due to the lack of experimental yield stresses as a function of ϕ and since S cannot be evaluated theoretically.

A simple model for the dependence of yield stress on the volume fraction of filler is presented in this work. This model for the yield stress is similar to the model used by Smith [7] for his analysis of the yield strain. In the case of "no adhesion" between filler and polymer the particles cannot carry any of the load. The load is carried only by the continuous phase, i.e. the polymer. A unit cube filled with n^3 uniformerly dispersed spherical particles is considered. Yielding is assumed to occur in the minimum cross section of the continuous phase which is perpendicular to the applied load, that is the cross section where the stress is at its maximum.

The minimum cross section Ap is given by

$$Ap = 1 - \pi(nr)^2 \tag{5}$$

and the volume fraction of spheres ϕ is equal to

$$\phi = \frac{4}{3} \cdot \pi (nr)^3 \tag{6}$$

Substitution of $(nr)^2$ from Equation (6) in Equation (5) gives

$$Ap = 1 - \pi\left(\frac{3}{4\pi}\right)^{2/3} \phi^{2/3} = 1 - 1.21\,\phi^{2/3} \tag{7}$$

and the yield stress of the composite σ_{yc} is equal to

$$\sigma_{yc} = \sigma_{yp}\,(1 - 1.21\phi^{2/3}) \tag{8}$$

where σ_{yp} is the yield stress of the unfilled polymer. In Equation (8) $\sigma_{yc} = \sigma_{yp}$ for zero concentration of filler and ϕ is equal to 0.75 for $\sigma_{yc} = 0$ which is the maximum theoretical packing where direct contacts are made between the particles. In practice the maximum packing that can be achieved by normal mixing techniques is about 0.64 while theoretically for hexagonal close-packed systems the maximum packing is 0.74.

In Figure 7 yield stress is plotted versus strain rate for three different concentrations of glass beads. Each curve was obtained by shifting data along the strain rate axis to the reference curve for 24°C. The upper curve in Figure 7 is obtained by dividing each experimental σ_{yc} value by $(1 - 1.21\phi^{2/3})$ according to Equation (8) and shifting to the curve for 24°C. The upper curve is shown to be practically independent of the glass bead concentration, and can be represented by the following equation:

$$\frac{\sigma_{yc}}{10^3\,(1 - 1.21\phi^{2/3})} = 10.2 + 0.3\,\ell n\,(\dot{\epsilon}\,a_T) \tag{9}$$

σ_{yc} is expressed in psi and $\dot{\epsilon}$ in min^{-1}. The shifting factors a_T were found to be practically independent of the filler concentration and $\ell n a_T$ values at 24, 48, 65 and 85°C are 0, -1.65, -3.46 and -6.13 respectively. Equation (9) describes all the experimental data that were obtained in this work, recalculated σ_{yc} values are

in a good agreement with the experimental values. The upper curve in Figure 7 and the right hand side of Equation (9) are both believed to describe the yield stress of th unfilled SAN. Obviously, since the unfilled polymer fails before reaching its yield stress, experimental values of σ_{yp} are not known. However the good agreement between calculated σ_{yp} values from data of different concentrations shown in Table 1, which summarizes typical calculated σ_{yp} values at 48°C for three rates of strain, supports this assumption. Fortunately, a few literature data on PPO/glass bead composites are available [8]. Unfilled PPO yields in tensile experiments therefore its experimental yield stress is known and can be compared with predicted σ_{yp} values calculated according to Equation (8). This comparison is shown in Table 2.

In this table the experimental yield stress of unfilled PPO is 780 kg/cm^2 which is in a good agreement with calculated σ_{yp} values from data for three different concentrations of glass beads. The applicability of Equation (8) has also been confirmed for data on polyester/glass bead composites [14].

In summary, in the case of no adhesion between filler and polymer, data on yield stress as a function of strain rate can be shifted along the yield stress axis to compensate for the filler effect and also along the strain rate axis to compensate for the temperature effect. A single master curve, that can be expressed analytically, describes the composite yield stress as a function of strain rate, temperature and filler content. The double shift procedure suggested in this work calls for additional confirmation with experimental data on other filler/polymer systems.

Acknowledgment

The authors express their gratitude to materials engineer R. E. Lavengood of Monsanto for his cooperation and advice.

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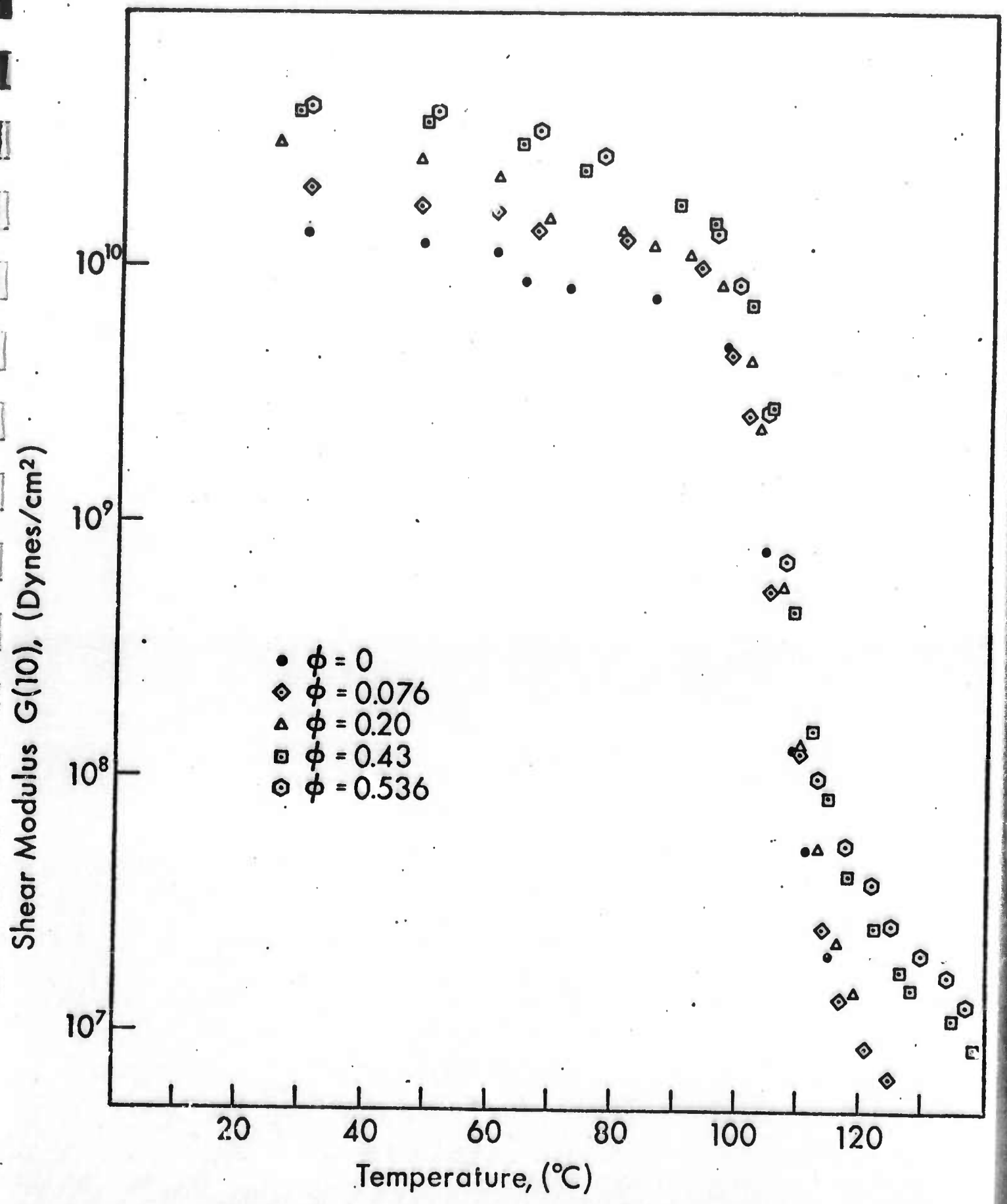
LIST OF FIGURES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10⁹
10⁸
10⁷
● ϕ = 0
◇ ϕ = 0.076
△ ϕ = 0.20
▫ ϕ = 0.43
⬡ ϕ = 0.536
20
40
60
80
100
120
Temperature, (°C)

Fig. 1

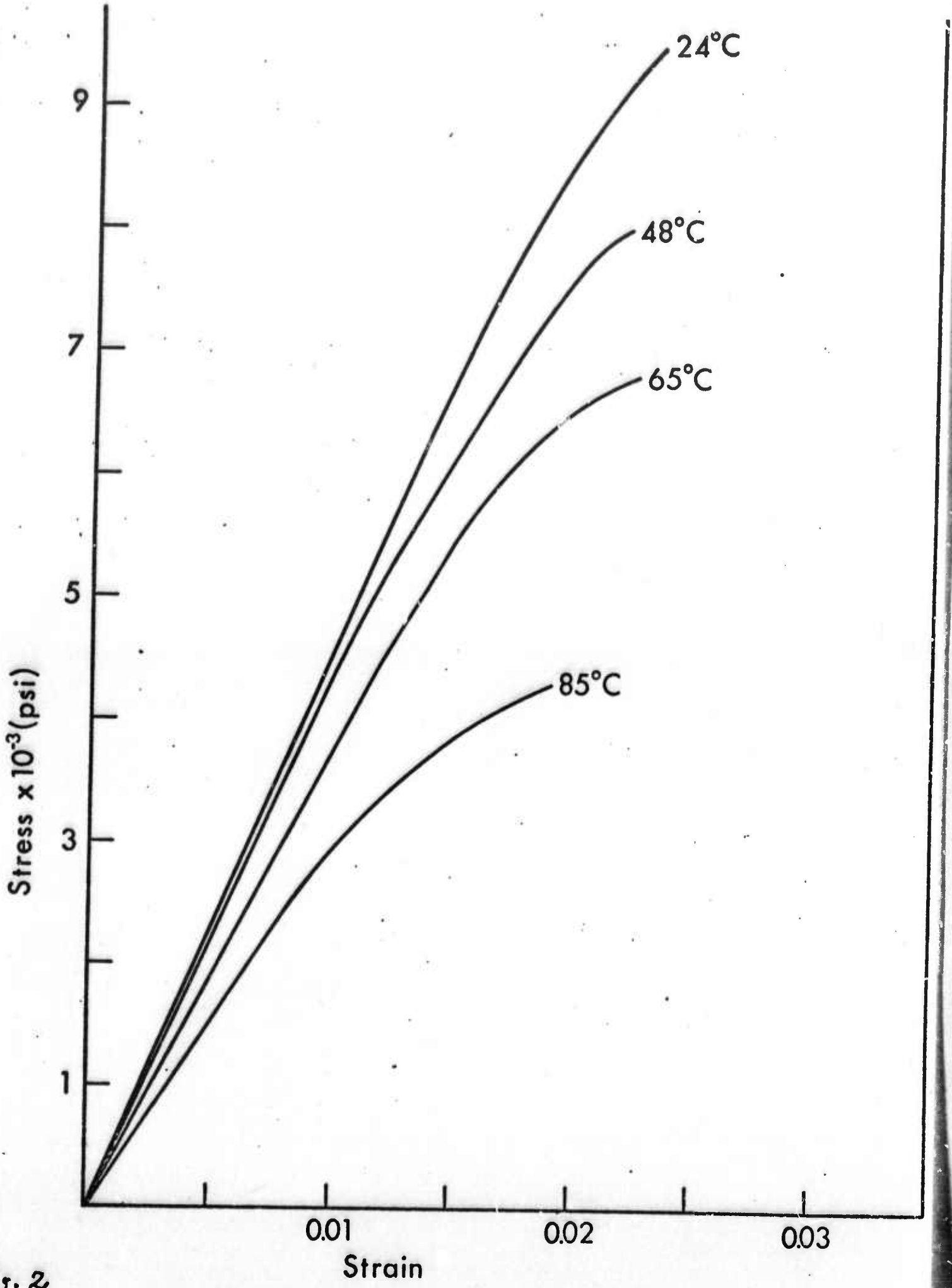


Fig. 2

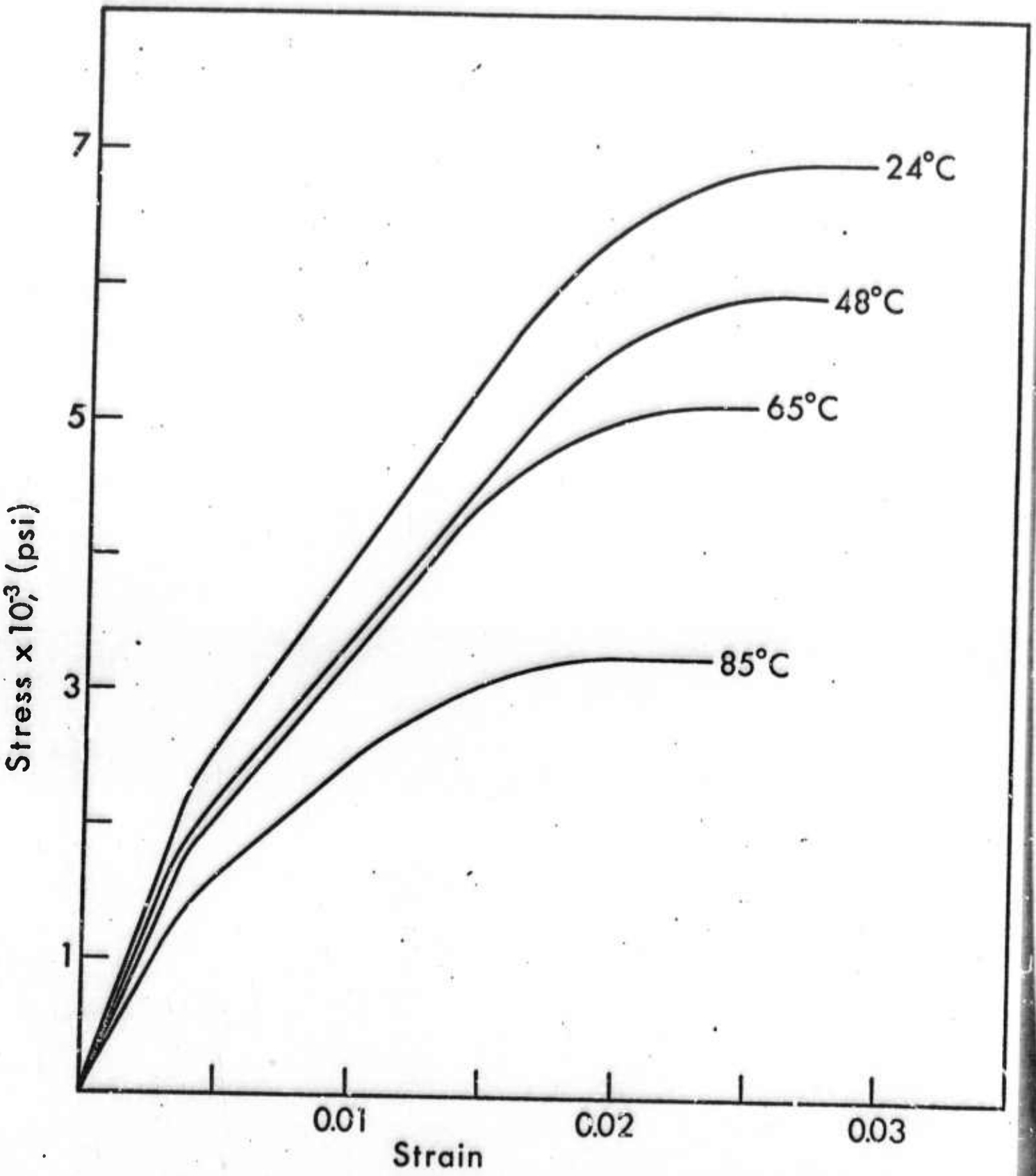


Fig. 3

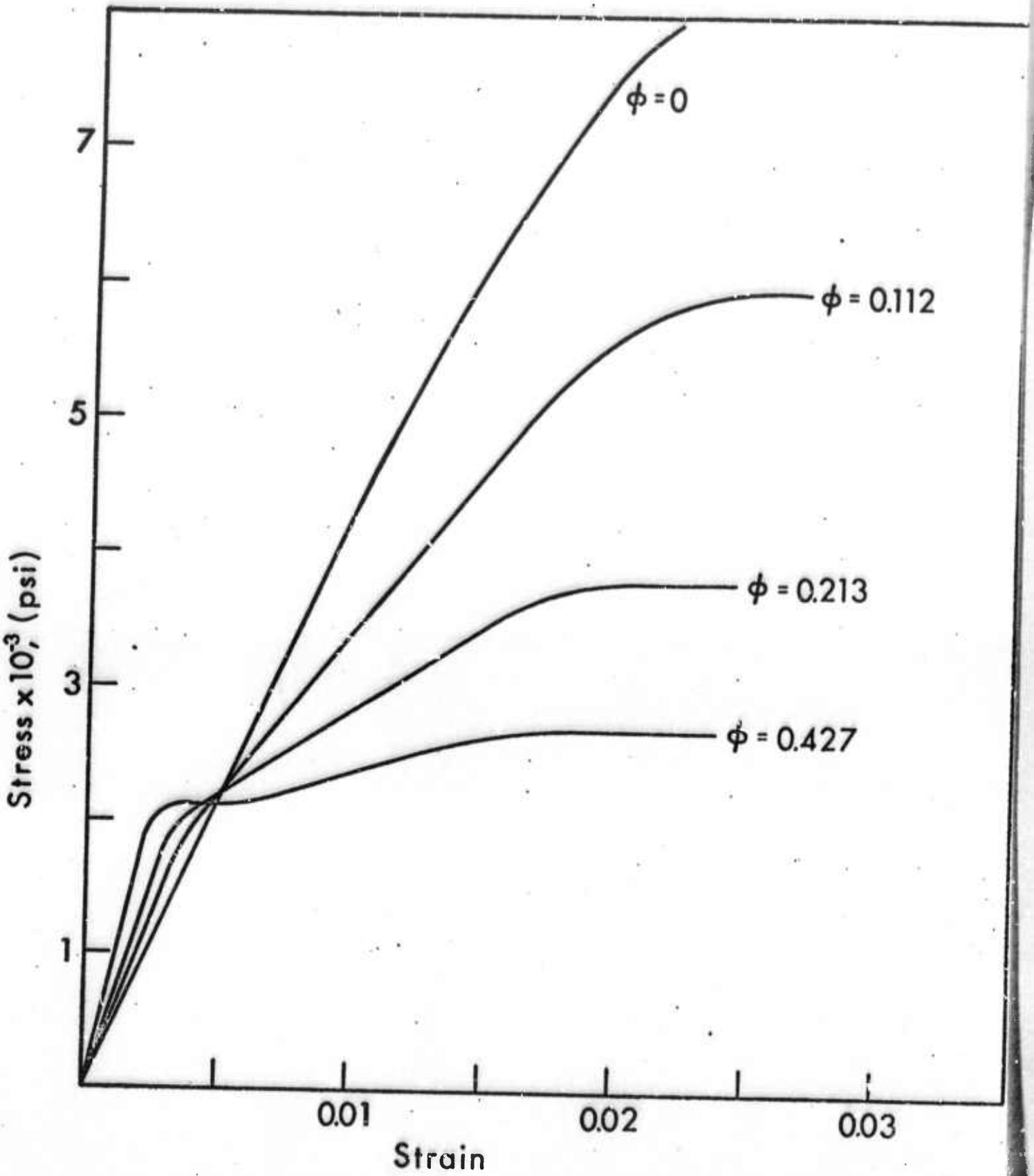

$\phi = 0$
$\phi = 0.112$
$\phi = 0.213$
$\phi = 0.427$
7
5
3
1
Stress x 10^3, (psi)
0.01
0.02
0.03
Strain

Fig. 4

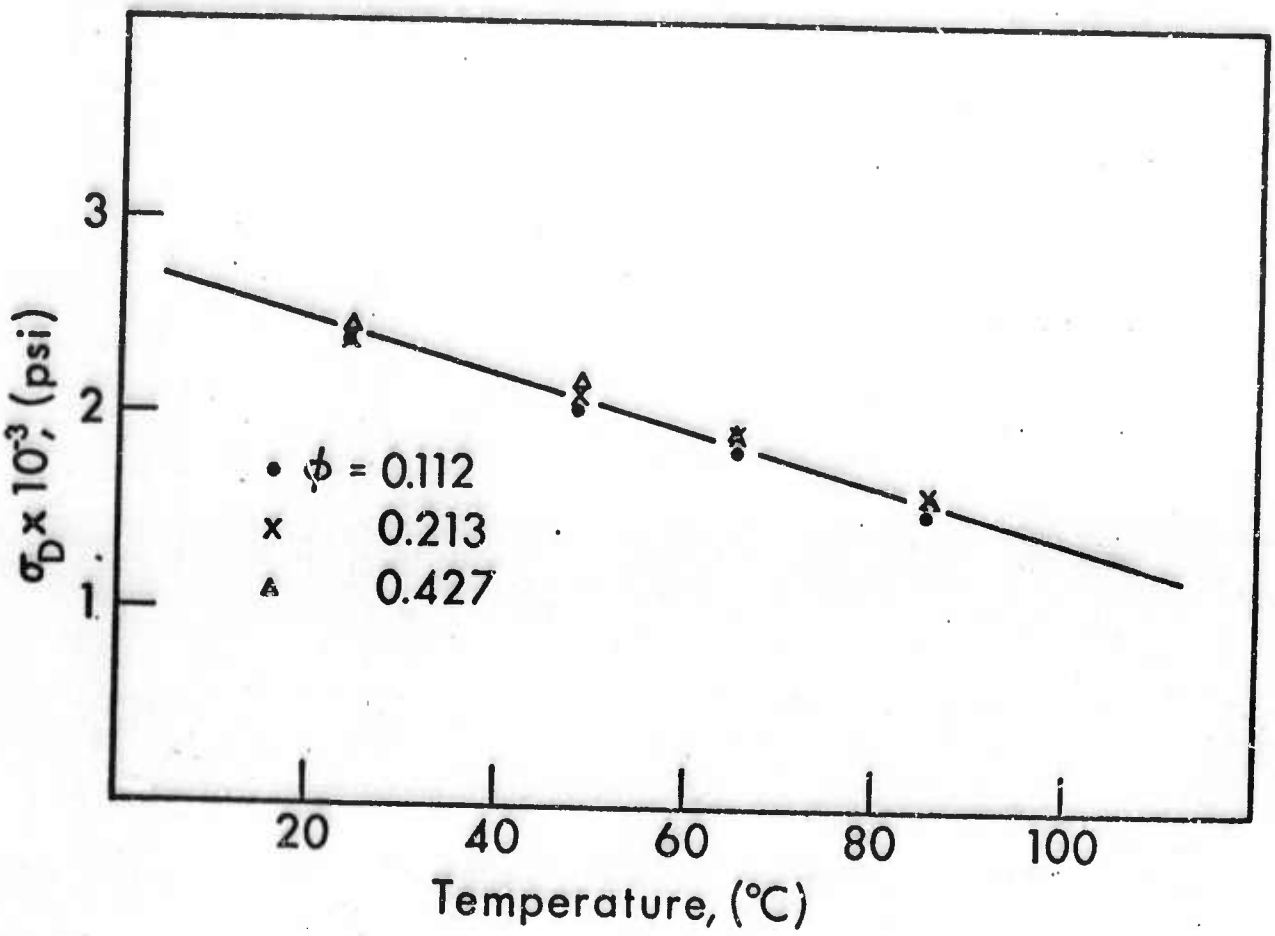

$\sigma_D \times 10^3$, (psi)
3
2
1
• ϕ = 0.112
x 0.213
▲ 0.427
20
40
60
80
100
Temperature, (°C)

Fig. 5

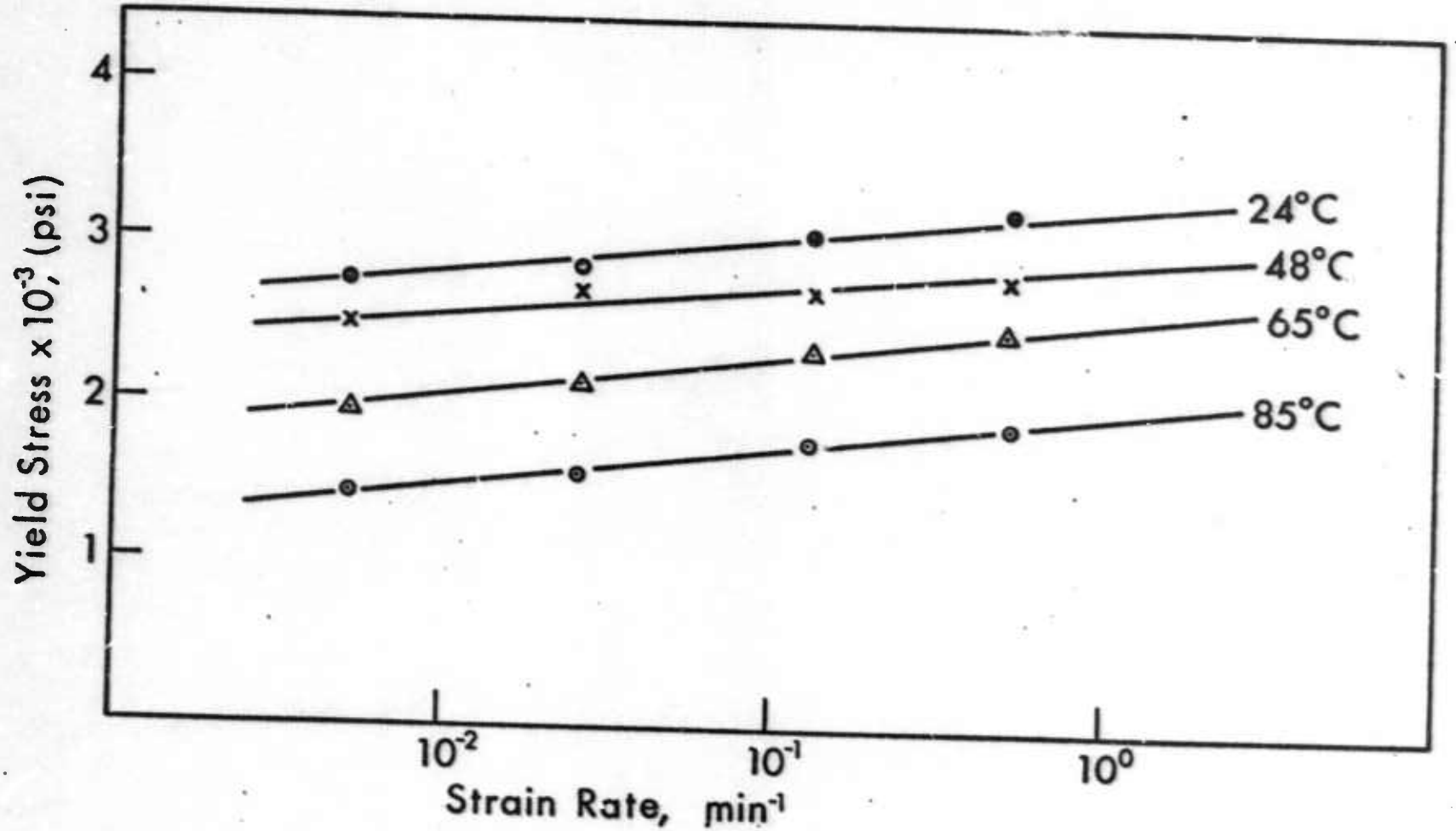
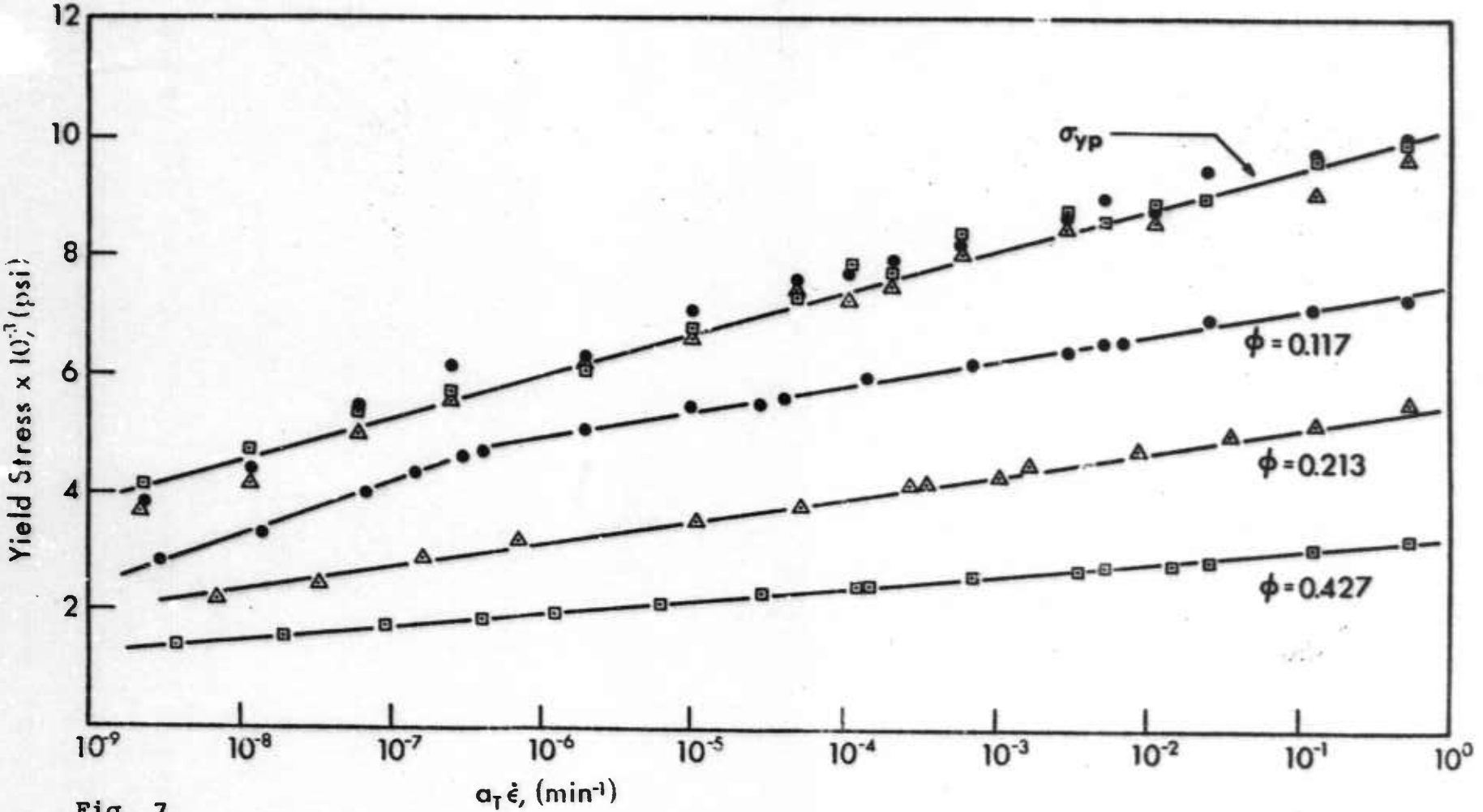

Yield Stress x 10^-3 (psi)
4
3
2
1
24°C
48°C
65°C
85°C
10^-2
10^-1
10^0
Strain Rate, min^-1

Fig. 6


12
10
8
6
4
2
Yield Stress x 10^{-3} (psi)
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ϕ = 0.117
ϕ = 0.213
ϕ = 0.427
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
$a_T \dot{\epsilon}$, (min^{-1})

Fig. 7

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13. ABSTRACT

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composites						
styrene-acrylonitrile						
strain rate						
yield stress						
modulus						
time-temperatura superposition						